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Note on a Besk programme for molecular one-electron two-center integrals and some diagrams showing the dependence of these integrals on the orbital exponents

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With 5 figures in the text

Introduction

The numerical treatment of the Schrödinger equation in quantum chemistry gives rise to molecular integrals of different kinds. The solving of these integrals is one of the most tedious problems in determining the energy levels of a certain molecule. Especially for crystals, where a large amount of atom neighbours must be taken into account, it is necessary to have a rapid way of computing these integrals.

For this purpose some of the most common one-electron integrals have been programmed by the present author for the Swedish electronic computer Besk. This programme is completely automatic and contains one-electron two-center integrals for all combinations of Slater atomic orbitals of the K, L and M shells. For integrals containing orbitals of higher electronic shells the programme is not applicable. Many of these integrals can, however, be rather easily computed by using the molecular functions $A_n(\alpha)$ and $B_n(\beta)$, which have been tabulated by the present author for $n \leqslant 8$ [1]. They can be given for a continuous range of values of the parameters α and β by the present programme and they are useful also for the computation of two-electron integrals. In an earlier note [2], the author has presented a programme for overlap integrals. This programme is included as a special case in the present programme.

Many excellent tables of molecular integrals have already been made by several other authors (e.g. Kopineck [3], Barnett and Coulson [4], Kotani *et al.* [5], Roothaan [6], Preuss [7], Müller, Gerhauser and Matsen [8] and many others). These tables also give other types of molecular integrals than those of the present programme. The Chicago group (Roothaan *et al.*) has also made extensive programmes for electronic computers containing all types of one-electron integrals and two-electron one-, two- and three-center integrals. All these integrals, however, contain only K and L shell orbitals. Thus the inclusion of M shell orbitals in the present programme will give some new material in addition to other available tables and programmes for electronic computers. The present programme has now been tested and used frequently for more than two years. Thus the probability that there still are cases for which the programme might fail is rather small.

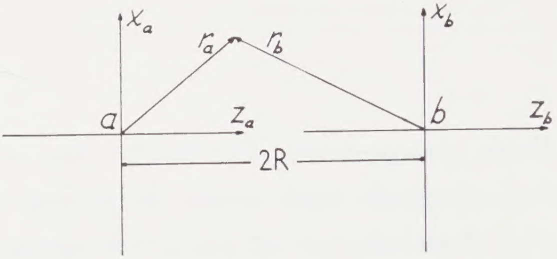

Fig. 1. Co-ordinate systems for the two nuclear centers *a* and *b*.

1. Description of the programme

The following types of one-electron integrals with two centers, *a* and *b*, can be computed by use of the programme:

A: Overlap integrals, $\int \psi_K^a \psi_L^b \, d\tau$.

B: Resonance integrals, $\int \psi_K^a \frac{1}{r_a} \psi_L^b \, d\tau$; $\int \psi_K^a \frac{1}{r_b} \psi_L^b \, d\tau$.

C: Kinetic energy integrals, $\int \psi_K^a \left(-\frac{1}{2}\Delta\right) \psi_L^b \, d\tau$.

D: Nuclear attraction integrals, $\int \psi_K^a \frac{1}{r_b} \psi_L^a \, d\tau$.

The molecular *A* and *B* functions

$$A_n(\alpha) = \int_1^\infty \xi^n e^{-\alpha\xi} d\xi, \quad B_n(\beta) = \int_{-1}^1 \eta^n e^{-\beta\eta} d\eta$$

can also be computed by use of the programme.

The orbital indices *K* and *L*[1] are used for indication of the integrals, and represent different nodeless hydrogen-like atomic orbitals of Slater type, according to the following table:

K:	0	1	2	3	4	5	6	7	8	9
ψ_K:	$1s$	$2s$	$2p\pi$	$2p\sigma$	$3s$	$3p\pi$	$3p\sigma$	$3d\delta$	$3d\pi$	$3d\sigma$

The nuclei are denoted by *a* and *b*, and the co-ordinate systems for the corresponding two centers have been chosen according to Fig. 1. We note that the two σ-directions (z_a and z_b) are chosen to be parallel. This means, for example, that the overlap integrals (13) and (31) have opposite signs. The same thing is true for resonance and kinetic energy integrals.

2. Use of the programme

The present programme is very simple to use and is available for everybody, who is interested in using it for computing molecular integrals.

There are three numerical parameters, which must be given for each integral, namely (cf. [2])

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[1] These indices do *not* correspond to the *K* and *L* shells.

R = *half* the inter-atomic distance
Z_K = effective charge of the K orbital
Z_L = effective charge of the L orbital

All these data values must be given in atomic units and put on the parameter tape in decimal form in the sequence given above and finally followed by the notation A. The decimal data values are written without decimal point and every value is followed by its sign notation (D for plus, B for minus) and the 10-exponent of its scale factor also with its sign notation (see example below).

After the data values the pertinent notation KL for the participating atomic orbitals and the notations $ABCD$ for the different types of integrals are written. If some of the integrals are not wanted, it is possible to exclude some of these notations. However, since the kinetic energy integrals, C, include linear combinations of A and B, the latter notations must always precede the notation C and cannot be excluded in order to get C correctly computed. For similar reasons, none of the notations A, B or C can be written after D.

The notations $ABCD$ are finally followed by the notation E, and another parameter scheme can be added. In the last parameter scheme, E must be replaced by F, which causes Besk to stop.

If the molecular A and B functions are wanted, the parameter scheme can be written as follows. At first the numerical data values of α and β, resp., must be written according to the decimal data rule, followed by the code notation A. Finally the notation AB is written. Then the scheme is finished and another one can be added. There is no certain final stop notation for this scheme.

The tape of the Besk programme, which has the notation $S3$, is available at *Matematikmaskinnämnden* in Stockholm. Together with the parameter tape, written according to the scheme above, it causes Besk to print an output which is described below.

The actual notation KL is printed to the left in the output and is followed by the data values R, Z_K and Z_L, written as ordinary decimal fractions. The values of the different integrals then follow, preceded by their pertinent notations. They are given with eight decimals together with the 10-exponents of their scale factors (see below). The notation B is followed by both the types of resonance integrals in the sequence given above.

As an example, we suppose that the B and D integrals of (28) are wanted for $R = 1.6251$, $Z_2 = 2.41$ and $Z_8 = 1$ and the same integrals of (16) for $R = 3.9233$, $Z_1 = 2.68$ and $Z_6 = 1.3$ (a.u.). The parameter tape must then be stamped as follows:

```
16251D1D   241D1D   1D1D   A   28   BD   E
39233D1D   268D1D   13D1D  A   16   BD   F
```

The corresponding output will be

```
28 1.6251 2.41 1     B −07025769 00    −04273470 00    D 09261602 -01
16 3.9233 2.68 1.3   B −14653864 00    −04161527 00    D 06612444 -01
```

This means that the first resonance integral of (28) (i.e. for $K = 2$, $L = 8$) for the given parameters is equal to -0.07025769 a.u., etc.

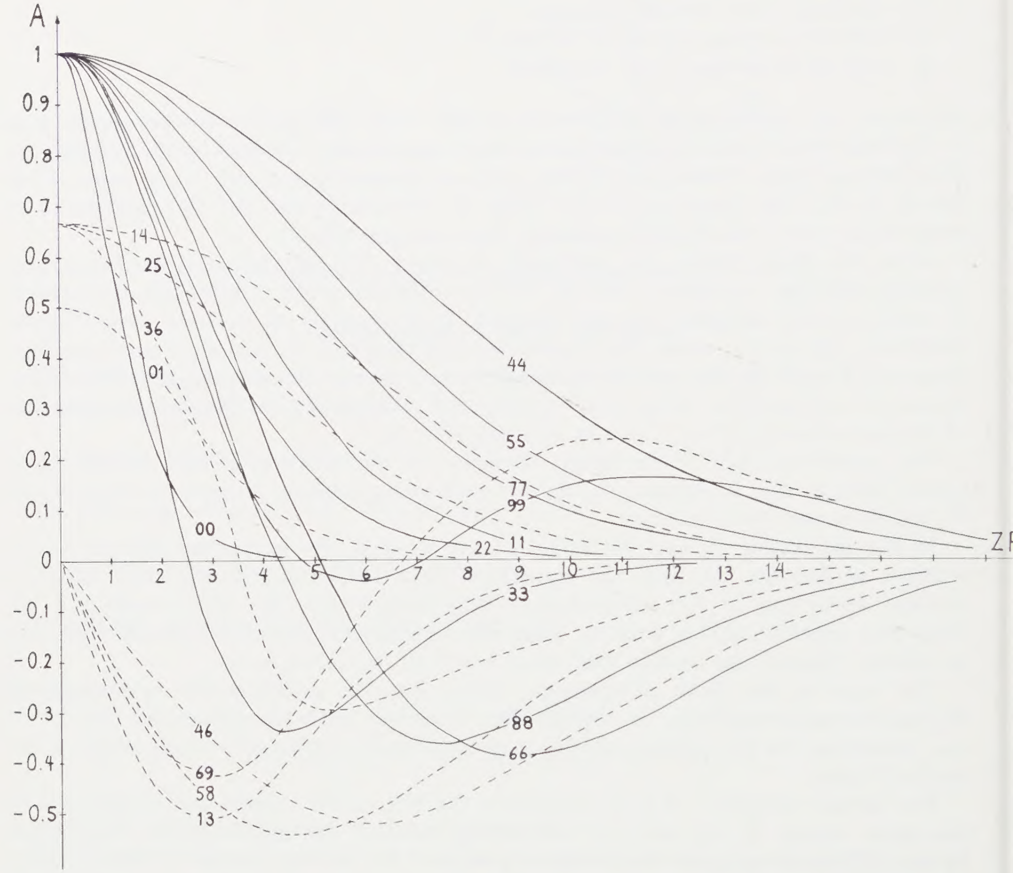

Fig. 2. Diagrams of overlap integrals, A, for orbitals with equal effective charges, Z (= principal quantum number times orbital exponent in a.u.), as functions of ZR (R = half the inter-atomic distance a—b in a.u.). The different curves are labelled by the two involved orbital indices K and L.

In the output for the molecular A and B functions the notation AB is printed, followed by the values of α and β. The A and B functions are then given in two tables, the left one giving $A_n(\alpha)$ and the right one $B_n(\beta)$ for $n = 0, 1, \ldots 8$, if $|\beta| \geqslant 2$, but only for $n = 0, 1, \ldots 6$, if $|\beta| < 2$.

3. Diagrams for some integrals of the *K*, *L* and *M* shells for equal exponents

As mentioned in section 2, the three parameters R, Z_a and Z_b are needed for the description of the two-center integrals. However, the overlap integrals, A, will remain unchanged, if R is divided by an arbitrary constant, k, at the same time as Z_a and Z_b are multiplied by k. In tabulating these integrals, thus only two parameters are needed. For example, these parameters can be chosen as RZ_a and RZ_b, or as one of these values and the ratio Z_b/Z_a.

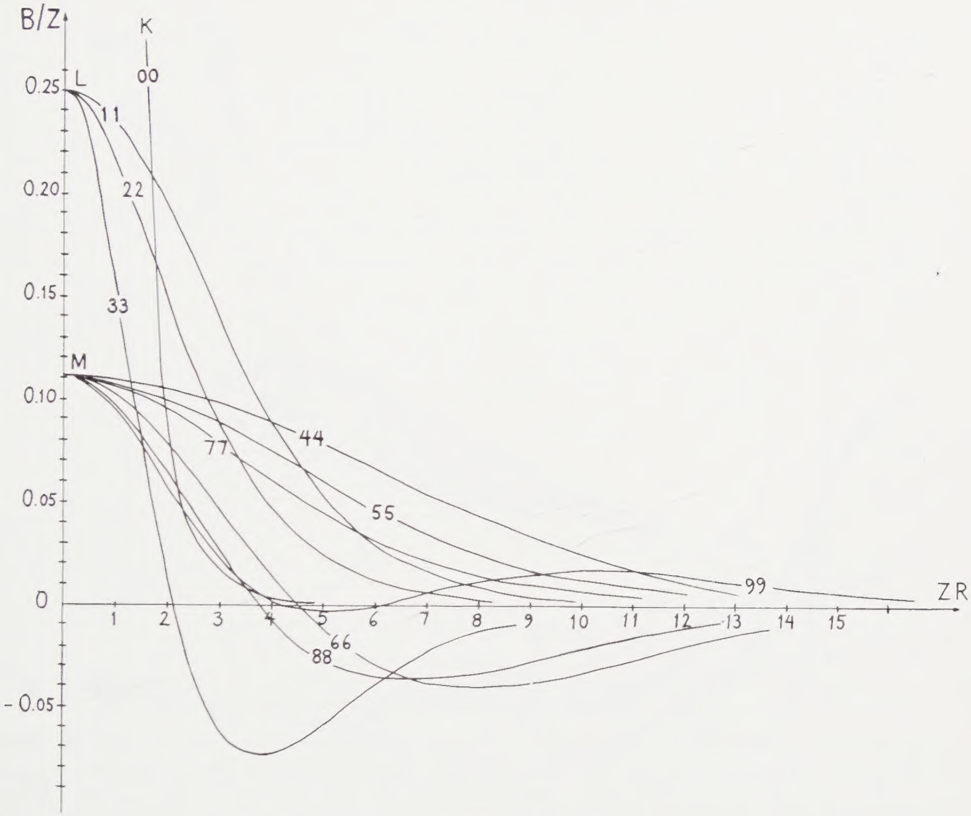

Fig. 3. Diagrams of B/Z as functions of ZR (equal Z). B = resonance integral (a.u.). Integral curves of the K, L and M shells have been plotted.

The other types of integrals are not invariant under transformations of this kind. However, there are certain simple connections between integrals transformed in this way, which makes it unnecessary to use more than two parameters for tabulating them. Choosing the constant k equal to R, we can write these connections for B and D integrals as

$$B\,(R,\,Z_a,\,Z_b) = \frac{1}{R}\,B\,(1,\,R\,Z_a,\,R\,Z_b);$$

and for C integrals as

$$C\,(R,\,Z_a,\,Z_b) = \frac{1}{R^2}\,C\,(1,\,R\,Z_a,\,R\,Z_b).$$

The diagrams given here correspond to equal effective charges, i.e. $Z_a = Z_b = Z$. Consequently, mainly diagonal integrals have been given. These integrals can be described by diagrams with only one parameter, $R\,Z$. The integrals for $Z = 1$ are found directly from the diagrams. The remaining integrals with equal effective charges, can be found by using the following formulae

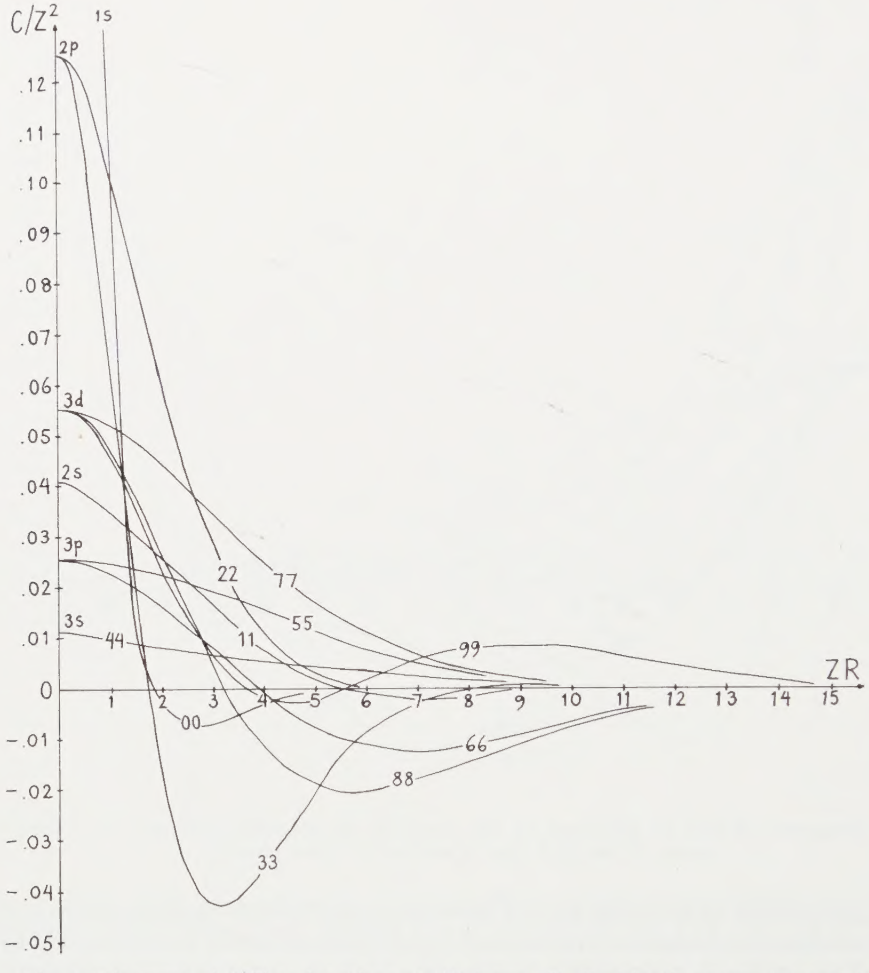

Fig. 4. Diagrams of C/Z^2 as functions of ZR (equal Z). C = kinetic energy integral (a.u.).

$$\begin{aligned} A\,(R,Z) &= A\,(RZ,1)\\ B\,(R,Z) &= Z\,B\,(RZ,1)\\ C\,(R,Z) &= Z^2\,C\,(RZ,1)\\ D\,(R,Z) &= Z\,D\,(RZ,1). \end{aligned}$$

The Figs. 2–5 show different diagonal integrals of the A, B, C and D types (for $Z=1$) as functions of the variable RZ. To find the corresponding integrals for $Z \neq 1$, the B and D values for $Z=1$ must accordingly be multiplied by Z and the C values by Z^2, while all the A integrals are found directly. Some non-diagonal overlap integrals combining equal and neighbouring shells have also been given, although these integrals might rather have been given with different effective charges.

It is interesting to notice the well-known fact that the different shells roughly correspond to different characteristic interaction ranges, which, however, also de-

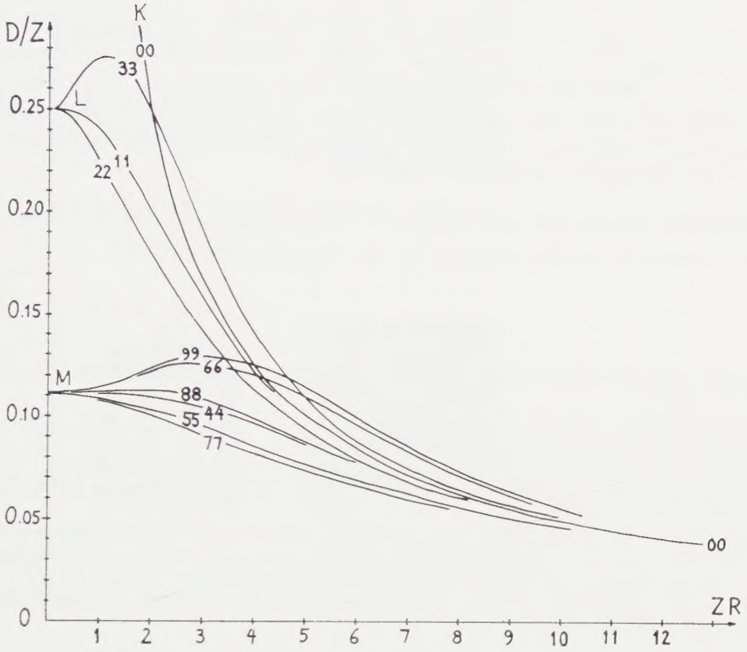

Fig. 5. Diagrams of D/Z as functions of ZR (equal Z). D = nuclear attraction integral (a.u.).

pend on the orbital exponents. By suitable choices of the orbital exponents these ranges can be made roughly equal for different shells. For example, if the ratio Z_M/Z_L of the Z-values for the M and L shells, resp., is chosen equal to about 2, this is seen to be the case for the L and M shells from Fig. 2. For physical reasons, however, the effective charges of the M shell orbitals of an atom would be less than those of the L shell orbitals, since M electrons would be more screened by the inner electrons than L electrons. Nevertheless, it might be of value to consider also the opposite case since physical pictures based on the conditions in the free atom are not always useful. These pictures may be applicable to atoms and small molecules, but for crystals they must not always be taken too literally. The use of Slater exponents for atomic orbitals of excited shells usually gives very large overlap for the nearest neighbours in a crystal and, consequently, bad convergence for the energy terms with increasing number of neighbours. Thus, the same orbital exponents as those found for atoms and molecules cannot always be used also for crystals. Actually, variation shows that much larger values often have to be used.

The diagrams given here are useful for finding the upper limit of atomic neighbours, which ought to be taken into account in energy band calculations for crystals.

As is seen from the diagrams, the shapes of the potential and kinetic energy integrals are rather similar to the shapes of the corresponding overlap integrals. However, they are far from proportional and their ratios sometimes even change their signs. Especially the kinetic energy integrals, C, differ rather much from being proportional to the overlap integrals, since they decrease more rapidly (for small Z values) with increasing argument, ZR. The functions D/Z all decrease as the inverse inter-atomic distance, $1/(2R)$, as is seen from Fig. 5. Consequently the approximation of considering overlap and energy elements as being proportional, frequently used in quantum chemistry, is far from satisfactory. However, using a suitable effective Hamiltonian operator for the system under consideration, the one-electron energy integrals given by the present programme, are useful for a rough calculation of the electronic states.

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